Poly[di(2-thiophenyl)carborane]s: conducting polymers with high electrochemical and thermal resistance.

Erhong Hao, Bruno Fabre, Frank R. Fronczek, M. Graça H. Vicente

Poly[di(2-thiophenyl)carborane]s: conducting polymers with high electrochemical and thermal resistance†‡

Erhong Hao,[a] Bruno Fabre,*[b] Frank R. Fronczek[a] and M. Graça H. Vicente*[a]

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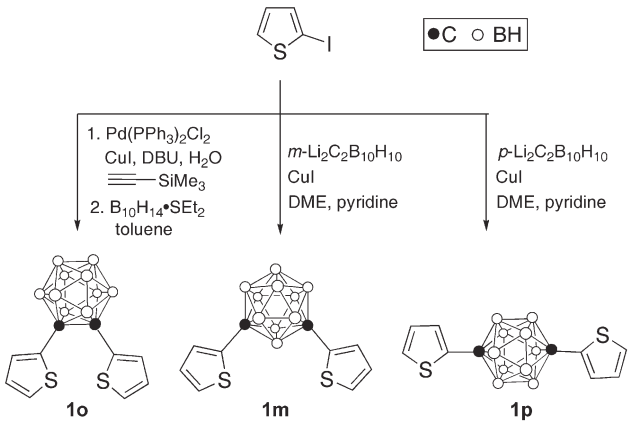
The synthesis, X-ray structure and electropolymerization of three new carbon–carbon linked di(2-thiophenyl)carboranes (1o, 1m and 1p) are reported; the resulting polymers bearing icosahedral *ortho*-, *meta*- or *para*-carborane clusters show high thermal and electrochemical stabilities in comparison with unsubstituted polythiophene; the *ortho*-carborane-containing polymer has the highest conductivity of the new materials.

Conjugated organic polymers, such as polythiophenes, are promising semiconducting materials with applications in sensory signal amplification, and in microelectronics, optoelectronics and electromechanical devices.[1–4] Therefore, the development of conducting organic polymers of high chemical and thermal stabilities is currently an active area of research.[5–8] In particular the introduction of bulky hydrophobic groups into the polymer backbone has been investigated as a means to improve the stability and performance of the polymers.[9] The icosahedral carborane clusters *o*-, *m*- and *p*-$C_2B_{10}H_{12}$ are attractive substituents as they are well-known for their electron-deficient nature, large molecular volume, high hydrophobicity, and high electrochemical and thermal stabilities. For example it has been shown that poly(carborane–siloxane)s have increased chemical and thermal stabilities compared with the unsubstituted parent polymers,[10–12] and that the introduction of the cobaltabisdicarbollide anion as doping anion,[13,14] or covalently bonded carborane clusters,[15,16] significantly improved the overoxidation threshold of the resulting polypyrroles. Herein we describe the synthesis and electropolymerization of three new carbon–carbon linked di(2-thiophenyl)carboranes (**1o**, **1m** and **1p**) to form polymers of high thermal and electrochemical stabilities. We anticipated that the three isomers bearing *ortho*-, *meta*- or *para*-carboranes, would produce polymers of defined geometry and conductivity.

Di(2-thiophenyl)carboranes **1o**, **1m** and **1p**, bearing respectively an *ortho*-, *meta*- or *para*-carborane group were synthesized from 2-iodothiophene as shown in Scheme 1. Compound **1o** was obtained in two steps, *via* the reaction of di(2-thiophenyl)acetylene with decaborane, in 24% overall yield. On the other hand, compounds **1m** and **1p** were prepared in a single step in 36 and 39% yields, respectively, *via* the coupling reaction of 2-iodothiophene with the dilithium salt of either *m*- or *p*-carborane, in the presence of cuprous iodide.[17] The structures of the three di(2-thiophenyl)carborane isomers were characterized by NMR, MS (see ESI‡) and by X-ray crystallography,§ as shown in Fig. 1. In all three structures, thiophenes exhibit the common disorder by twofold rotation about the thiophene-carborane C–C bonds, swapping S and C positions. The *o*-isomer has two independent molecules, one having an ordered thiophene and a 56 : 44 disordered one, the other having an ordered thiophene and a 90 : 10 disordered one. The *m*-isomer has crystallographic C_2 symmetry, with the thiophene disordered 78 : 22. The *p*-isomer has crystallographic inversion symmetry, with thiophene disordered 75 : 25.

All three compounds **1o**, **1m** and **1p** were readily oxidized electrochemically to form the corresponding polymer films, at oxidation potentials that increased in the order **1o** < **1m** < **1p** (Table 1). The lower oxidation potential required in the case of **1o** made it more favorable in the electropolymerization process, by overcoming the so-called "polythiophene paradox" and achieving high conductivity. Typical cyclic voltammograms corresponding to the potentiodynamical electropolymerization of **1o** are shown in Fig. 2. The electrochemical response of the electrogenerated polymers showed the same trend as that observed for the monomers, namely the formal potential decreasing in the order poly(**1o**) < poly(**1m**) < poly(**1p**). Among them, poly(**1o**) shows the highest doping level (0.50) (Fig. 3), which is associated with the formation of largest population of bipolaron charge carriers. The generation of bipolaron charge carriers largely reduced the π–π*



Scheme 1 Synthesis of di(2-thiophenyl)carboranes.

[a]*Department of Chemistry, Louisiana State University, Baton Rouge, LA, 70803, USA. E-mail: vicente@lsu.edu; Fax: 225-578-3458; Tel: 225-578-7405*
[b]*Matière Condensée et Systèmes Electroactifs MaCSE, Sciences Chimiques de Rennes, Unité Mixte de Recherche n° 6226 CNRS/ Université de Rennes 1, Campus de Beaulieu, 35042, Rennes Cedex, France. E-mail: bruno.fabre@univ-rennes1.fr; Fax: 33-22323-6732; Tel: 33-22323-6550*

† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Synthetic procedures, electrochemistry, UV-visible spectroscopy and conductivity data. See DOI: 10.1039/b710375a

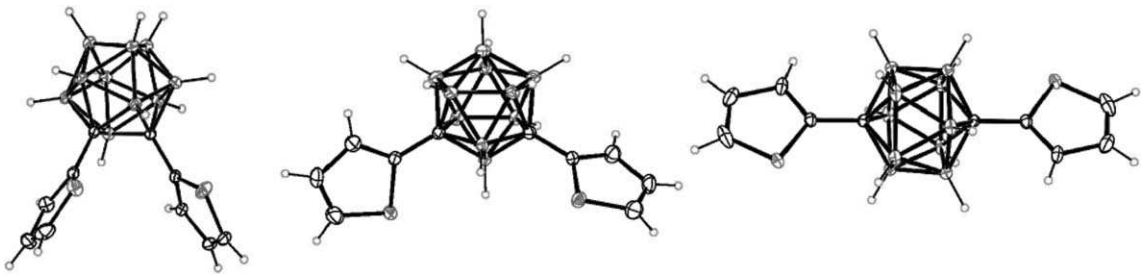


Fig. 1 X-Ray crystal structures of **1o**, **1m** and **1p**, with 50% probability for the ellipsoids. Only the major conformer of each disordered thiophene is shown.

Table 1 Cyclic voltammetry data of **1o**, **1m** and **1p** at 10^{-2} M in CH_2Cl_2 + 2 × 10^{-1} M Bu_4NPF_6. Potential scan rate: 0.1 V s^{-1}

	$E_{pa\ mon}$[a]/V	$E^{\circ\prime}{}_{poly}$[b]/V	δ[c]	λ_{max}[d]/nm
1o	0.90; 1.70; 2.15	0.52	0.50	528; 565; 615
1m	1.11; 1.84; 2.18	0.87	0.07	488
1p	1.12; 1.82; 2.06	1.14	0.06	425

[a] Irreversible anodic peak potentials corresponding to the monomer oxidation. [b] Formal potential corresponding to the reversible p-doping/undoping of the electrogenerated polythiophene (average of anodic and cathodic peak potentials). [c] The doping level δ is the number of positive charge per monomer unit and has been calculated from the anodic charge Q_a under the polymer voltammetric response following $\delta = 2Q_a/(Q_s - Q_a)$ where Q_s is the electropolymerization charge. [d] Position of the maximum absorption of the solid-state neutral polymer.

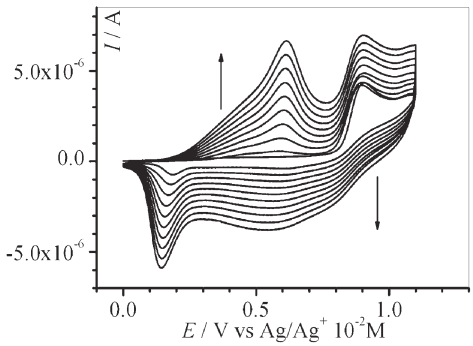


Fig. 2 Successive cyclic voltammograms at 0.1 V s^{-1} of **1o** at 10 mM in CH_2Cl_2 + 0.2 M Bu_4NPF_6.

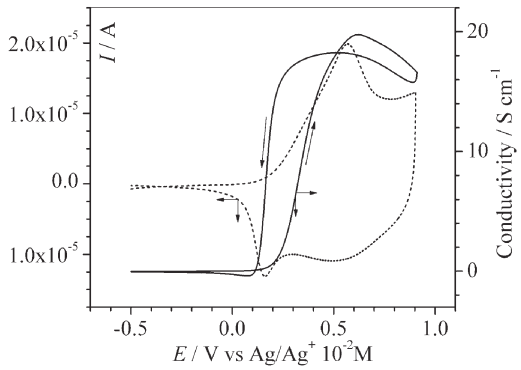


Fig. 3 Electrochemical response of poly(**1o**) (dashed line) and conductivity *vs.* potential (solid line) at 0.02 V s^{-1} in CH_2Cl_2 + 0.2 M Bu_4NPF_6.

band gap, and response for the high conductivity of polymers.[18] Thus poly(**1o**) is expected to be more conjugated and consequently more conducting than the other two related polymers (*vide infra*).

The above results were supported by the UV-visible spectroscopy analysis of the polymers in their neutral and p-doped forms (Fig. 4 and ESI‡). In the neutral form, the three polymers display similar absorptions, with *ca.* 100 nm red shifts in the order poly(**1o**) > poly(**1m**) > poly(**1p**). Importantly, the neutral poly(**1o**) shows a well-defined vibronic fine structure with maxima at 528, 565 and 615 nm. Such optical features which are not observed for poly(**1m**) and poly(**1p**) are typical of highly conjugated, ordered polymers.[19] A similar shifting is also observed for the oxidatively doped polymers that display a new longer wavelength band at 810, 730 and 686 nm for poly(**1o**), poly(**1m**) and poly(**1p**) respectively. All these differences indicate that the incorporation of *o*-carborane into the polymer backbone causes a more efficient reduction of the π–π* energy gap compared with the *m*- and *p*-carboranes. For the three doped polymers, a further broad band attributed to the formation of the so-called "free carrier tail"[20] is also visible in the near IR region at >1000 nm.

In agreement with the UV-visible data, the *in situ* conductivity measurements of these polymers also show a clear dependency on the carborane isomer used. The conductivity profiles for poly(**1m**) and poly(**1p**) show maximum values of ~12 S cm^{-1} at 0.9 and 1.2 V *vs.* Ag/Ag^+ respectively. For poly(**1o**), the conductivity reaches a quasi-plateau at much less positive potentials (0.6 V) with conductivities near 20 S cm^{-1} (Fig. 3). Furthermore, poly(**1o**) showed high electrochemical stability and only a slight decrease in conductivity up to 1000 cycles. Again, the *in situ* conductivity data confirmed that the *o*-carborane cluster conferred the highest

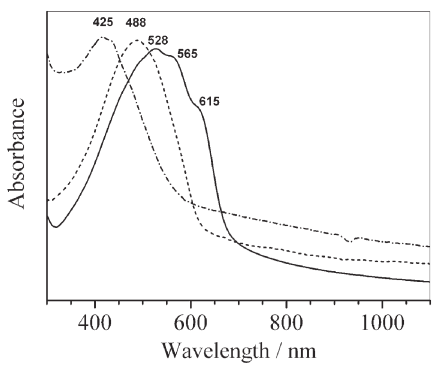


Fig. 4 Solid-state UV-visible spectra of undoped poly(**1o**) (solid line), poly(**1m**) (dashed line) and poly(**1p**) (dash-dotted line).

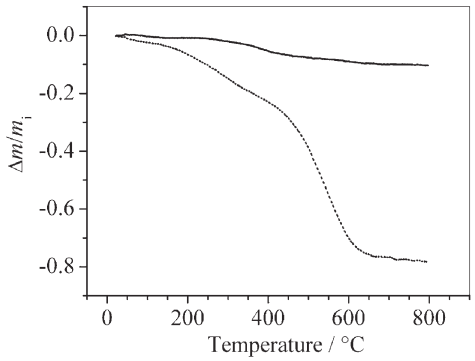


Fig. 5 TGA analysis of undoped poly(**1o**) (solid line) and polythiophene (dashed line) under N_2. Mass of polymer: 3 mg; heating rate: 10 °C min^{-1}.

conductivity to the parent polymer of the three carborane isomers studied. The shape of the relationship of conductivity with potential suggested there was possibly mixed-valence conduction, as previously observed in polypyrrole, as a contribution to the bipolaron conduction.[21] This would correspond to an equal concentration of polarons and bipolarons at the maximum conductivity.

The more conjugated and ordered structure of poly(**1o**) compared with poly(**1m**) and poly(**1p**) could be explained by a more planar conformation of the conjugated backbone resulting from an intramolecular β–β′ cyclization reaction in the monomer. Molecular modeling calculations using the DFT method are currently in progress to test this hypothesis.

The integration of carborane cages into the polymer backbone was also found to dramatically increase the thermal stability of the polymers. As an example, the thermogravimetric analysis (TGA) of undoped poly(**1o**) is shown in Fig. 5. The TGA was performed under N_2 up to 800 °C. Compared with TGA of polythiophene, there is only a slight loss in the mass of poly(**1o**), less than 10% up to 800 °C. For the parent polymer, there was a continuous loss in mass reaching ~80% at 600 °C.

In summary we report the preparation of new poly[di(2-thiophenyl)carborane]s bearing either *ortho*-, *meta*- or *para*-carborane clusters. These materials show very high thermal and electrochemical stabilities in comparison with parent polythiophene. We show that the nature of the carborane groups strongly influences the conductivity of the resulting polymers. In particular the incorporation of *o*-carborane showed the greatest conductivity. Therefore a new design of conducting polymers with high electrochemical and thermal stabilities *via* the incorporation of *o*-carboranes into the conjugated polymer backbone has been developed.

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Notes and references

§ *Crystallographic data*: **1o** at 90 K: $C_{10}H_{16}B_{10}S_2$, triclinic, space group $P\bar{1}$, a = 10.3905(12), b = 12.330(2), c = 12.5115(15) Å, α = 81.871(7), β = 89.204(7), γ = 81.639(7)°, V = 1569.9(4) $Å^3$, Z = 4, D_c = 1.305 g cm^{-3}, 40732 reflections collected with θ <30.9°, 9669 unique; $R1$ = 0.047, $wR2$ = 0.124 refined on F^2, CCDC 650330; **1m** at 90 K: $C_{10}H_{16}B_{10}S_2$, monoclinic, space group $C2/c$, a = 19.019(4), b = 7.3765(10), c = 13.170(3) Å, β = 122.216(7)°, V = 1563.2(5) $Å^3$, Z = 4, D_c = 1.311 g cm^{-3}, 11174 reflections collected with θ <32.9°, 2865 unique; $R1$ = 0.038, $wR2$ = 0.103, CCDC 650331; **1p** at 90 K: $C_{10}H_{16}B_{10}S_2$, monoclinic, space group $P2_1/c$, a = 7.1753(10), b = 7.3908(10), c = 15.103(2) Å, β = 102.266(6)°, V = 782.65(18) $Å^3$, Z = 2, D_c = 1.309 g cm^{-3}, 17113 reflections collected with θ <33.7°, 3040 unique; $R1$ = 0.039, $wR2$ = 0.104, CCDC 650332. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710375a

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